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COMPLETE SPECIFICATION

Improvements relating to Polyurethane Elastomers

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyurethane elastomers having improved freeze resistant properties.

Polyurethane elastomers prepared from polytetramethylene ether glycol of molecular weight about 1000, a stoichiometric excess of an arylene diisocyanate, and an arylene diamine are known for their outstanding physical properties and toughness, and also possess relatively good low temperature properties. Attempts to prepare softer polyurethane elastomers based on polytetramethylene ether glycol of a higher molecular weight have been partially successful, but it has been found that such elastomers have poor freeze resistance on long-term exposure to temperatures in the neighbourhood of -20°C . Thus, while they show fair freeze resistance on a short term basis, they become increasingly hard upon prolonged exposure to low temperature. This is very detrimental to their application for industrial equipment which may be subjected to extremely low temperatures as often encountered in winter operations. The poor freeze resistance of these polymers is believed to result from crystallisation involving the polytetramethylene ether glycol portion of the polymer backbone.

Similar polyurethane elastomers can be prepared from polypropylene ether glycol having a molecular weight in the range 1000—2000. Compared to the polytetramethylene ether glycol polyurethane elastomers, the polypropylene ether glycol analogues are much softer, lower in resilience, and more sensitive to

moisture, and generally lack the toughness required for many uses. While the polypropylene ether glycol-based polyurethanes have less tendency to crystallise during prolonged storage at -20°C ., they do stiffen at temperatures even above 0°C . to such an extent as to reduce their usefulness especially when lower molecular weight polypropylene ether glycols (e.g. 1000) are employed. This stiffening of polypropylene ether glycol-based polyurethanes generally limits their application at lower temperatures.

According to the present invention polyurethane elastomers are made by reacting together in any order (1) about 15 to 50 percent (by weight of the total glycol) of a polypropylene ether glycol of average molecular weight about 900 to 4000, (2) about 85 to 50 percent (by weight of the total glycol) of a polytetramethylene ether glycol of average molecular weight about 1800 to 3000, (3) as a diisocyanate reactant toluene-2,4-diisocyanate or a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate, and (4) an arylene diamine having a pK_b of at least 9.7 and having both amino radicals directly attached to aromatic nuclei, 1.5—2.5 moles of diisocyanate being used for each mole of glycol, and 0.85—1.05 moles of diamine being used for each mole of diisocyanate in excess of the stoichiometric equivalent of the glycol.

A critical feature of the invention is the use of the specified mixtures of polytetramethylene ether glycol and polypropylene ether glycol of the specified molecular weights. If the molecular weight of the polytetramethylene ether glycol is above about 3000, the polyurethane elastomers formed have a greater tendency toward crystallisation on long-term storage at low temperatures. On the other hand, elastomers derived from polytetramethylene ether glycol of molecular weight below about 1800 tend to stiffen at low temperature to a greater extent than the elastomers of the present invention. Similarly the

use of polypropylene ether glycol of molecular weight below 900 results in an elastomer which shows undue stiffness at low temperature. Polypropylene ether glycol having a molecular weight greater than about 4000 probably could be used; however, the higher the molecular weight of a polypropylene ether glycol, the more difficult it is to prepare it in high enough quality to make it suitable for use in elastomers.

The proportions of the two glycols used are likewise important in giving excellent low temperature properties while retaining physical properties which are generally acceptable for most applications. Elastomers prepared from mixtures containing less than 15 percent polypropylene ether glycol tend to be deficient in freeze resistance over extended periods of time due to crystallisation, while elastomers prepared from mixtures which contain over 50 percent by weight polypropylene ether glycol begin to have much of the stiffness of straight polypropylene ether glycol-based elastomers and, in addition, physical properties and toughness start to drop toward those of pure polypropylene ether glycol-based elastomers. The elastomers which may be derived from glycol blends containing about 20—35 percent by weight of polypropylene ether glycol and 80 to 65 percent by weight of a polytetramethylene ether glycol are especially preferred because they do not give evidence of crystallisation on long-term storage at -20°C . and show very little more stiffness than do elastomers derived exclusively from polytetramethylene ether glycol. In addition, elastomers prepared from these preferred glycol blends retain most of the excellent physical properties and toughness normally associated with polytetramethylene-ether glycol-based elastomers. Glycol blends made up of 30% by weight of polypropylene ether glycol of average molecular weight 1000—2000 and 70% by weight of polytetramethylene ether glycol of average molecular weight 2000 are especially suitable.

The glycols required for the preparation of the elastomers may be made by conventional means. Polytetramethylene ether glycol is usually prepared by polymerising tetrahydrofuran in the presence of an acid catalyst, and polypropylene ether glycol by polymerisation of propylene oxide in the presence of basic catalysts.

As the diisocyanate reactant a mixture containing 80% 2,4-isomer and 20% 2,6-isomer is especially preferred because it is readily available commercially, but pure 2,4-isomer or the mixture containing 65% 2,4-isomer and 35% 2,6-isomer, both of which are commercially available, may also be used.

About 1.5 to 2.25 moles of toluene diisocyanate are employed per mole of glycol mixture, i.e. 1.5 to 2.25 isocyanate groups for each hydroxyl group. Elastomers containing less diisocyanate tend to be deficient in physical

properties and lack toughness. Also, if a prepolymer process is used in preparing the elastomers, the prepolymers containing less than 1.5 moles of isocyanate per mole of glycol will generally be too viscous to permit easy handling and curing. If more than 2.25 moles of diisocyanate per mole of glycol is used, low temperature stiffness tends to rise.

The final component required for the preparation of the elastomers is the arylene diamine. The restriction in regard to pKb, which is an indication of basicity, is necessary because more basic amines, having pKb's of less than 9.7, cause such rapid reaction of isocyanato groups that premature gelling is usually encountered before mixing of all reactants can be completed. While amines having pKb's of about 9.7 can be used successfully in the present invention, amines of lower basicity are often more convenient to use. The preferred amine is 4,4'-methylenebis-(2-chloroaniline), which is often used as a curing agent for isocyanate-terminated prepolymers. Other suitable diamines include compounds such as 3,3'-dichlorobenzidine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylthioether, and 4,4'-isopropylidenebis-(2-chloroaniline). The arylene diamines are employed in amounts of 0.85 to 1.05 moles per mole of stoichiometrically excess isocyanate; i.e. the amount, in moles, of diamine employed is 0.85 to 1.05 times the difference between the number of moles of diisocyanate and the number of moles of glycol. For example, if two moles of diisocyanate are used with one mole of mixed glycols, the excess of diisocyanate amounts to one mole and the arylene diamine should be employed in amount 0.85 to 1.05 moles. When more than about 1.05 mole of diamine per mole of excess diisocyanate is employed, the physical properties of the final elastomer are often found wanting, because such excesses of diamine prevent the polymer from reaching a sufficiently high molecular weight. When less than about 0.85 moles of diamine per mole of excess diisocyanate are employed, considerable cross-linking is present in the final polymer, and thus is usually detrimental to physical properties.

The reactants required to prepare the elastomers of the present invention, namely polytetramethylene ether glycol, polypropylene ether glycol, toluene diisocyanate and arylene diamine, may be combined in several ways. For example, all four reactants, along with suitable catalysts, may be mixed continuously in a high speed mixing head, and the resulting mixture introduced into moulds or suitable containers for curing. Prepolymer techniques may also be employed, and in general are preferred. The prepolymer route involves reacting the individual glycols or their blends with the required amount of toluene diisocyanate as a first step. If the individual glycols are reacted with toluene diisocyanate, the required com-

position is produced by blending proper proportions of prepolymers. The glycol-diisocyanate reaction is usually carried out by adding the glycol or glycol blend to the diisocyanate in an agitated vessel, keeping the temperature below about 80°C. When all of the glycol has been added to the diisocyanate, the temperature is adjusted to about 80°C. and so maintained for 3—12 hours. The exact time needed depends on the glycols involved; thus the hold period need only be 3—4 hours when polytetramethylene ether glycol alone is involved, but a 10—12 hour holding period is preferred when only polypropylene ether glycol is involved because the secondary hydroxyl groups contained in this glycol are slower reacting than the primary hydroxyl groups of polytetramethylene ether glycol. A particularly convenient procedure for preparing prepolymers of blended glycols consists in adding the polypropylene ether glycol to all of the toluene diisocyanate, and then adding the polytetramethylene ether glycol at 80°C. over about two hours, after which the charge is heated for 6 hours at 80°C. to complete the reaction. As when all the reactants are mixed simultaneously, certain catalysts which are known to change the rate of the OH—NCO reaction may be employed in making the prepolymers. Such catalysts include stannous 2-ethylhexanoate, dibutyl tin dilaurate and ferric acetylacetonate. In preparing finished elastomers by the prepolymer route, the prepolymer and the required amount of arylene diamine curing agent are mixed intimately, and once the mixture is homogeneous it is placed in a mould or other suitable container and allowed to cure. Prior to mixing the prepolymer with the arylene diamine, it is customary to de-gas the prepolymer by heating under vacuum for a short time. Generally, the arylene diamine will be added to the de-gassed prepolymer in the form of a liquid. The preferred arylene diamine, 4,4'-methylenebis-(2-chloroaniline), may be heated in an oven at or above 115°C. The arylene diamine can also be added to the prepolymer in the form of a finely divided solid, and the resulting mixture placed in a mould and heated to cause melting of the arylene diamine which automatically will bring about cure. While curing will take place slowly at room temperature, it is customary to accelerate the rate of cure by heating to about 100°C. Using temperatures of about this level, acceptable cures can be obtained in times ranging from about 30 minutes to 5 hours. A preferred curing period is 3 hours at 100°C.

The elastomers of the invention find use in making a variety of cast articles. Their outstanding low temperature properties suit them for use in moulded mechanical goods such as gaskets and solid tyres for lorries which may be subjected to low temperatures for extended periods of time.

The following Examples illustrate the invention; parts are by weight unless otherwise indicated.

EXAMPLE 1

A series of five prepolymers and their corresponding vulcanizates are prepared from polytetramethylene ether glycol of molecular weight about 2,000, polypropylene ether glycol of molecular weight about 1,000, toluene-2,4-diisocyanate and 4,4'-methylenebis-(2-chloroaniline). Two of these prepolymers are prepared respectively from pure polytetramethylene ether glycol and pure polypropylene ether glycol, and are included for comparison. The other three prepolymers and their vulcanizates differ mainly in the ratio of polytetramethylene ether glycol to polypropylene ether glycol employed. In all cases, the amount of toluene-2,4-diisocyanate used in making the prepolymer is such that the prepolymers contain 4.0 to 4.2% by weight of isocyanato groups. The proportions of the glycols and isocyanate are given in the Table below. The prepolymers are prepared by adding the glycol or glycol blend as required to the proper amount of toluene diisocyanate contained in an agitated reaction vessel which may be heated or cooled as required. Addition of the glycol to the isocyanate is performed as rapidly as possible without allowing the temperature to exceed 80°C. Once all the glycol has been added, the reaction mixture is maintained at a temperature of about 80°C. for 10 hours except in the case of the prepolymer prepared from pure polytetramethylene ether glycol, which is only held for 4 hours. Upon completion of heating, the prepolymers are cooled to about room temperature and stored out of contact with moisture until required for use.

The prepolymers are converted to cured elastomers by the addition of 90% of the theoretical amount of 4,4'-methylenebis-(2-chloroaniline) required to react with all of the free isocyanate groups contained in the prepolymers. The amounts of the arylene diamine curing agent used are also given in Table I. Before the addition of the curing agent, the prepolymers are heated to about 85°C. and degassed under vacuum at 10 mm. pressure for about 15 minutes. While the prepolymer is still at an elevated temperature, the required amount of curing agent in molten form at a temperature of about 115°C., is added quickly and intimately mixed into the prepolymer. The resulting mixture may be cast into any mould, but in this Example it is cast into a mould which forms sheets or slabs of the elastomer which are suitable for testing purposes. The mixtures of prepolymer and diamine are cured by holding the moulds in a 100°C. oven for about 3 hours. The slabs are then removed from the moulds and are ready for testing. The usual physical properties are measured on the five elastomers and, in addition, a

low temperature test for freeze resistance is also carried out by measuring hardness as a function of time of low temperature storage.

An increase in hardness is an indication of crystallization. The results of these measurements are presented in Table I.

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TABLE I

Polypropylene ether glycol, % by weight of polyether glycol mixture the remainder being polytetramethylene glycol	0*	20	33.3	50	100*
Mole ratio toluene diisocyanate/polyether glycol mixture	2.25	2.0	1.85	1.80	1.64
Parts 4,4'-methylenecbis (2-chloroaniline)/100 parts prepolymer	10.7	12.48	11.32	11.95	11.71
Tensile strength, psi.	4750	4200	4550	3940	2260
Extension at break, %	440	440	490	510	540
Modulus at 300% extension, psi	1880	1575	1190	1010	580
Resilience (Yerzley)	70	61	63	65	32
Hardness (Shore A)	81	78	77	68	51
Freeze Resistance at -20°C.					
Hardness (Shore D) after					
0 days	40	39	39	40	62
5 days	43	39	39	40	65
10 days	46	39	39	40	66
20 days	49	38	38	41	68
30 days	50	38	38	41	70
40 days	50	38	38	42	70

* These polyurethane elastomers are outside the scope of the invention.

The physical properties presented in Table I illustrate the deficiencies of pure polypropylene ether glycol based elastomers relative to polytetramethylene ether glycol based elastomers and those prepared from blends containing up to 50% by weight polypropylene ether glycol. The blends containing 20, 33.3 and 50% polypropylene ether glycol, and especially those containing 20 to 33.3%, show excellent physical properties and outstanding low temperature properties.

EXAMPLE 2

About 690 parts of polytetramethylene ether glycol having a number average molecular weight of about 2000 is added to 115 parts of toluene-2,4-diisocyanate contained in an agitated reaction vessel. During the glycol addition, the temperature is not allowed to exceed 80°C. Following the glycol addition, the reaction mass is held for 4 hours at a temperature of about 80°C. The prepolymer is then cooled to room temperature and stored

until required. It is designated Prepolymer A.

A second prepolymer, Prepolymer B, is prepared by adding about 654 parts of polypropylene ether glycol of molecular weight about 1000 to 196 parts of toluene-2,4-diisocyanate contained in an agitated reactor. Following the glycol addition, the reaction mass is heated at about 80°C. for 10 hours. It is then cooled to room temperature and stored until required.

Cured elastomers designated I and II are prepared from the prepolymers as follows:

Elastomer I—About 90 parts of Prepolymer A is mixed with 10 parts of Prepolymer B and the mixture is cured with 10.55 parts of 4,4'-methylenecbis(2-chloroaniline) by the mixing and curing procedure described in Example 1.

Elastomer II—About 80 parts of Prepolymer A is mixed with 20 parts of Prepolymer B and cure is effected by the procedure of Example 1 with about 10.9 parts of 4,4'-methylenecbis(2-chloroaniline).

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The freeze resistance for both Elastomers I and II is given below. Elastomer I does not contain the required minimum amount of 15% by weight polypropylene ether glycol based on

the total weight of polyether glycol present and is deficient in respect to freeze resistance as indicated by the following data:

	Days exposure at -20°C	Hardness (Shore D)	
		Elastomer I	Elastomer II
10	0	35	34
	4	37	34
	11	46	34
	18	44	34
	25	46	35

EXAMPLE 3

About 774 parts of polypropylene ether glycol of molecular weight 1000 is added to about 480 parts of an isomer mixture of toluene diisocyanate (80%, 2,4-; 20%, 2,6-) contained in an agitated reactor equipped for heating and cooling. The temperature during the addition is maintained at 76—80°C. While maintaining the same temperature, 1800 parts of polytetramethylene ether glycol of about 2000 molecular weight is added over a period of 2.5 hours. Following this latter addition, the reaction mass is held at about 80°C. for 4 hours and then cooled to room temperature and stored in air-tight containers until required. The prepolymer is converted to an elastomer by intimately mixing 100 parts of degassed prepolymer at a temperature of about 85°C. with 9.4 parts of molten 4,4'-methylenebis(2-chloroaniline) at a temperature of about 100°C. The mixture is cured to the finished elastomer at 100°C. for 3 hours. The cured elastomer has the following properties:

40	Tensile strength, psi.	3200
	Extension at break, %	680
	Modulus at 300% extension, psi	720
	Resilience (Yerzley)	67
	Hardness (Shore A)	77
45	NBS Abrasion Index	90
	Freeze Resistance at -20°C.	
	Hardness (Shore D) after	
	0 days	32
	6 days	32
50	9 days	32
	14 days	32
	22 days	32
	25 days	32

EXAMPLE 4

About 100 parts of polypropylene ether glycol (2000 molecular weight) is added to 51.5 parts of an isomer mixture of toluene diisocyanate (80%, 2,4-; 20%, 2,6-) contained in an agitated reaction vessel equipped for heating and cooling. This addition is followed by an addition of about 50 parts of polytetramethylene ether glycol of molecular weight 2000. The reaction mixture is heated to 75—80°C. Then an additional 183.5 parts of the

polytetramethylene ether glycol is added over two hours at a temperature of 80°C. The entire mixture is then held at 78—80°C. for 6 hours, after which it is cooled to room temperature and stored in dry airtight containers.

The prepolymer is converted to a vulcanized elastomer by the procedure employed in Example 3 with the exception that 8.8 parts of 4,4'-methylenebis(2-chloroaniline) are used.

The properties of this elastomer are as follows:

75	Tensile strength, psi.	3600
	Extension at break, %	740
	Modulus at 300% extension, psi	740
	Resilience (Yerzley)	69
	Hardness (Shore A)	77
80	NBS Abrasion Index	100
	Freeze Resistance at -20°C.	
	Hardness (Shore D) after	
	0 days	34
	5 days	35
85	10 days	35
	20 days	35

WHAT WE CLAIM IS:—

1. Process for the production of polyurethane elastomers, which comprises (1) reacting together in any order 15 to 50 percent (by weight of the total glycol) of a polypropylene ether glycol of average molecular weight 900 to 4000, (2) 85 to 50 percent (by weight of the total glycol) of a polytetramethylene ether glycol of average molecular weight 1800 to 3000, (3) as a diisocyanate reactant toluene-2,4-diisocyanate or a mixture of toluene-2,4-diisocyanate and toluene-2,6-diisocyanate, and (4) an arylenediamine having a pKb of at least 9.7 and having both amino radicals directly attached to aromatic nuclei, 1.5 to 2.5 moles of the diisocyanate reactant being used for each mole of glycol, and 0.85 to 1.05 moles of diamine being used for each mole of diisocyanate in excess of the stoichiometric equivalent of the glycol.

2. Process according to claim 1, wherein the polypropylene ether glycol makes up 20 to 35 percent by weight, and the polytetramethylene ether glycol 80 to 65 per cent by weight, of the total glycol.

